English Equivalent for JP 51-24377

PATENT SPECIFICATION

(11) 1393078

1393078

(21) Application No. 58447/73 (22) Filed 18 Dec. 1973

(31) Convention Application No. 126200/72 (32) Filed 18 Dec. 1972 in (19)

(33) Japan (JA)

(44) Complete Specification published 7 May 1975

(51) INT CL² C08G 77/04//C08L 83/04

(52) Index at acceptance

C3T 6D11 6D12 6D2A 6D5 6D9 6F2 6G7F 6G7K 6G8 6H4D 6K2C 6K5 6K8B 6K8C

C3S 7A 7B 8 P2X

(54) ORGANOPOLYSILOXANE COMPOSITION HAVING IMPROVED HEAT STABILITY

(71) We, TORAY SILICONE COMPANY LTD., a company organised under the laws of Japan of Yaesu-Tatemono Building, 6—1, 2-chome, Hatechobori, Chuo-ku, Tokyo 104, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to cerium silioxanolates and to organopolysiloxane compositions based on essentially linear polymers which contain cerium siloxanoates and exhibit improved heat stability. Specifically, this invention relates to silicone fluids and silicone elastomers containing cerium siloxanolates which exhibit improved stability when exposed to elevated temperatures.

It has been well known to improve the heat stability of organopolysiloxane compositions by incorporating therein certain inorganic salts of metals including iron, zirconium, cerium, manganese and nickel. Particularly with respect to the cerium compounds, it has been known to incorporate cerium oxides, cerium hydroxides and cerium salts of aromatic carboxylic acids in organopolysiloxane compositions as shown in Japanese Patent No. 283,598 and in Japanese Patent No. 535,121. However, these metal salts and metal compounds as described above require incorporation into the organosiloxane composition in the form of a pre-compounded paste. The metal salt is first formed into a paste in a portion of the organopolysiloxane or a solution in an organic solvent because the metal compound *per se* is not readily compatible with or easily mixed into the organopolysiloxane composition. Even when the metal compounds are so pre-mixed with an organic solvent or an organopolysiloxane, the resulting solution or paste is difficult to disperse uniformly and satisfactorily throughout the organopolysiloxane composition and the desired heat stabilizing effect is not realized.

The failure of the cerium compounds employed in the prior art to impart the desired degree of heat stability is clearly seen in the failure to impart heat stability to organopolysiloxane fluids having relatively low viscosities when an organic or inorganic salt of cerium, as set forth above, is incorporated in a lower viscosity organopolysiloxane fluid, the cerium compound forms an incompatible sediment and separates from the fluid.

In order to overcome the defects noted above, it has been proposed in U.S. Patent No. 3,008,901 to dissolve or colloidally disperse in the organopolysiloxane composition a cerium compound prepared by heating a mixture of a specific cerium complex with organopolysiloxane fluids containing a small proportion of hydrogen atoms bonded to silicon (SiH) in an aromatic hydrocarbon solvent at 280° to 290°C. for 1 to 4 days while bubbling air through the reaction mixture. However, even when such a method is employed to prepare the cerium compound, it is found that only a very small proportion of the resulting cerium material is compatible with the organopolysiloxanes. Further, it has proven difficult to determine the proportion of cerium actually added to the organopolysiloxane because the wide fluctuation of reaction conditions employed results in an inconsistent and generally uncontrolled cerium compound. Of course, the lack of consistency in the chemical composition of the additive results in inconsistent results in the ultimate product containing the cerium compound as a heat stability additive. This is obviously a serious defect insofar as large scale commercial production of such materials is concerned.

The primary object of this invention is to prepare organopolysiloxane compositions exhibiting significantly improved heat stability using a cerium compound of consistent quality which is compatible with and easily dispersed in organopolysiloxane fluids and elastomer compounds.

Accordingly the present invention provides a method for improving the heat stability of

organopolysiloxanes which comprises adding thereto the reaction product of a cerium salt of an organic carboxylic acid which is soluble in an aromatic hydrocarbon solvent or a chlorinated hydrocarbon solvent with an alkali metal siloxanolate having an average of at least three organosiloxane units per molecule.

This invention employs the reaction product of (1) a cerium salt of an organic carboxylic acid and (2) an alkali metal siloxanolate having an average of at least three organosiloxane units per molecule as a heat stability additive in organopolysiloxanes based on essentially linear organopolysiloxanes and more particularly organosiloxane fluids and elastomers based on essentially linear diorganopolysiloxanes. The reaction product of a cerium carboxylate and alkali metal siloxanolate is compatible with the organosiloxane compositions and imparts superior heat stability to the products.

The organopolysiloxanes employed in this invention are essentially linear polymers preferably of the unit formula

$$R_nSiO_{\frac{4-n}{2}}$$

where n has an average value of 1.98 to 2.01 and R is a monovalent hydrocarbon or halogenated hydrocarbon radical having from 1 to 30 carbon atoms, preferably methyl, ethyl, propyl, 3,3,3 - trifluoropropyl, phenyl and vinyl radicals. These polymers are well known in art and are predominantly diorganosiloxanes (R_2SiO) with minor amounts (less than ten mol percent) of $R_3SiO_{1/2}$ units, $RSiO_{3/2}$ units and $SiO_{4/2}$ units. The terminal groups on the linear polymers can be, *inter alia*

$$HOR_2SiO_{1/2},$$

$$R_3SiO_{1/2},$$

$$\text{alkoxy } R_2SiO_{1/2}$$

or

$$CH_2{=}CHR_2SiO_{1/2}.$$

The viscosity of the polymer can vary from very thin fluids (e.g. 1 cs. at 25°C.) to gum-like materials (e.g. 10^6 cs/at 25°C.). All of these materials are well known, prepared by known methods and many are commercially available.

The heat stability additive employed herein is the reaction product of a cerium salt of an organic carboxylic acid which is soluble in an aromatic hydrocarbon or chlorinated hydrocarbon solvent, such as cerium 2-ethylhexoate and cerium naphthoate with an alkali metal siloxanolate such as potassium and sodium siloxanolates having an average of at least three siloxane groups per molecule.

The preferred alkali metal siloxanolates are potassium dimethylsiloxanolate, sodium dimethylsiloxanoate, potassium methylphenylsiloxanolate, sodium methylphenylsiloxanote, or an essentially linear diorganosiloxane wherein the organic radicals bonded to the silicon are methyl, ethyl, phenyl, vinyl or 3,3,3 - trifluoropropyl groups, one of the terminating units being an alkali metal siloxanolate unit and the other terminating unit being a triorgano siloxy unit wherein the organic substituents are defined above.

The alkali metal siloxanolates can be prepared by known methods as illustrated by Grubb and Osthoff in the Journal of the American Chemical Society, Vol. 77, page 1405 (1955). The alkali metal siloxanolates so prepared have silanolate groups ($MOSi\equiv$ where M is alkali metal) at both ends of an essentially linear molecule and can be further rearranged to form alkali metal siloxanolates having silanolate groups on one end of the polysiloxane chain by reaction with other linear organopolysiloxanes. These later "monofunctional" alkali metal siloxanolates are preferred reactants herein.

Aromatic hydrocarbon solvents and chlorinated hydrocarbon solvents are preferred as the reaction medium in which the cerium salt of carboxylic acid is reacted with the alkali metal siloxanolate. However, mixtures of aromatic hydrocarbon solvents or chlorinatel hydrocarbon solvents with other organic solvents can be employed.

The reaction of the cerium salt with the alkali metal silixoanclate is accelerated by heating the reaction mixture. Preferably, the reaction is carried forward at the reflux temperature of the reaction mixture. Small amounts of catalysts such as dialkyl-formamide or hexa-alkylphosphoramide can be employed.

The proportion of alkali metal siloxanolate to cerium salt in the reaction mixture is not critical but best results are achieved with a reaction mixture containing 1 to 5 alkali metal siloxanolate groups for each cerium atom in the reaction mixture.

Reaction begins with the mixing of the reactants in the organic solvent medium and will be completed within 30 minutes to 24 hours depending upon reaction temperature. After the reaction is completed, the organic solvent is removed and any precipitates generated are removed by filtration. The desired reaction product is usually obtained as a liquid which can be easily and uniformly dissolved in or dispersed in organopolysiloxanes. Further, by selecting an alkali metal siloxanolate having the appropriate number and species of organosiloxane units in accordance with the chemical structure of the organopolysiloxanes in which the reaction product is to be employed, extreme compatibility of the additive with the organopolysiloxane can be insured. This excellent compatibility

results in transparent fluids and elastomers exhibiting excellent heat stability.

The cerium content of the reaction product employed herein is usually 0.5 to 5% by weight based on the weight of the reaction product. It is preferred to employ the reaction product in the organopolysiloxane fluid or elastomer in proportions such that the ultimate product contains from 0.01 to 1.0% by weight of cerium based on the weight of the ultimate product. However, diminished heat stability can be realized below the 0.01% level of cerium and the lack of change in clarity or colour of the product is generally achieved with from 0.01% to 0.1% by weight of cerium added.

The cerium reaction product prepared as described above can be added to organosiloxane fluids and organosiloxane gums which are compounded with known fillers such as silicas and mixed with metal soaps or pigments, and heat vulcanizable or room temperature vulcanizable silicone rubber compositions having improved heat stability can be prepared by compounding the composition of this invention with organic peroxides such as benzoyl-peroxide, 2,4 - dichlorobenzoyl-peroxide and t - butylperoxide or with known crosslinkers such as alkyl silicates, triacetoxysilane, trioximesilane and methylhydrogenpolysiloxane and known curing catalysts such as tin salts of fatty acids and platinum compounds together with inorganic fillers.

The cerium carboxylate-alkali metal siloxanolate reaction products are compatible and dispersible in organopolysiloxanes so that small amounts of the reaction products incorporated in organopolysiloxanes will impart heat stability characteristics equivalent to the characteristics achieved with much larger amounts of previously known heat stibility additives such as cerium oxides. Further, the process for incorporating the heat stability additive of this invention is much simpler because of the compatibility and/or solubility of the cerium siloxanolate in the organopolysiloxane. This, of course, is a great advanage for commercial operations.

The following Examples illustrate the invention.

Example 1

33 g. of potassium siloxanolate prepared by known methods from potassium hydroxide, hexamehylcyclotrisiloxane and octamethylcyclotetrasiloxane and 0.3 g. of hexamethyl phosphoramide were added to 6.7 g. of trimethylsilyl terminated dimethylpolysiloxane having a viscosity of 20 cs. at 25°C. The mixture was heated at 115°C. for 1 hour under a nitrogen stream. 120 g. of dry xylene and 16 g. of cerous 2-ethylhexoate were added to the reaction mixture which was then heated at reflux temperature for 2.5 hours.

After cooling the reaction mixture to room temperature, 3 g. of trimethylchlorosilane were added to neutralize the catalyst. The reaction product (R_1) was a light yellow liquid obtained after evaporation of the solvent under reduced pressure and filtration to remove precipitates. The cerium content of R_1 was 1.2% by weight.

4.5 grams of reaction product R_1 was added to 150 grams of dimethylpolysiloxane fluid having a viscosity of 350 cs. at 25°C. and the mixture was placed in a 300 ml. glass beaker. The reaction product R_1 dissolved readily and uniformly in the polymer by simple stirring. This mixture was labelled Sample A.

For comparison purposes, Sample B was prepared and consisted of 150 grams of the same dimethylpolysiloxane employed in Sample A.

Samples A and B were placed in an air circulating oven heated to 300°C. After seven hours, Sample B had gelled. Sample A did not gel even after 24 hours at 300°C. in the air circulating oven and the viscosity of Sample A had increased only to 420 cs. at 25°C.

Example 2

Following the method set forth in Example 1 for preparing reaction product R_1 cerium naphthoate was employed in place of the cerous 2-ethylhexoate to produce reaction product R_2 containing 1.1% by weight of serium.

0.25 g. of reaction product R_2 was uniformly dispersed in 10 g. of a copolymer of 60 mol percent phenylmethylsiloxane units and 40 mol percent of dimethylsiloxane units, the copolymer having a viscosity of 350 cs. at 25°C. The mixture was labelled Sample C and placed in a 50 ml. glass beaker. The control (Sample D) was 10 g. of the same phenylmethylsiloxane - dimethylsiloxane copolymer in a 50 ml. glass beaker.

Samples C and D were placed in an air circulating oven heated at 300°C. Sample D gelled after 67 hours at 300°C. in the oven and sample C had not gelled after 180 hours in the oven at 300°C.

Example 3

100 g. of potassium siloxanolate prepared as described in Example 1 was mixed with 12 g. of cerous 2-ethylhexoate dissolved in 150 g. of dry xylene. The mixture was heated at reflux temperature for 3 hours under nitrogen.

The reaction mixture was cooled to room temperature and 3 g. of trimethylchlorosilane were added to neutralize the unreacted potassium silanolate. The reaction product R_3 was a light yellow liquid obtained after distilling off the solvent under reduced pressure and filtering to remove the generated precipitates.

The cerium content of reaction product R_3 was 1.1% by weight.

In a 50 ml. glass beaker, there was placed 10 g. of dimethylpolysiloxane having a viscosity of 100 cs. at 25°C. and 0.1 g. of reaction product R_3 was easily dissolved in the dimethylpolysiloxane. This mixture was Sample E. The control, Sample F, consisted of 10 g. of the same dimethylpolysiloxane employed in Sample E and placed in a 50 ml. glass beaker.

Samples E and F were placed in an air circulating oven heated at 250°C. Sample F had gelled after 24 hours in the oven and had a weight loss of 11.7% by weight. Sample E did not gel even after 48 hours in the oven and had a weight loss of only 6.5% after 48 hours.

Example 4

100 parts by weight of an organosiloxane copolymer gum having a Williams plasticity of 150 as measured by Japanese Industrial Standard C-2123, the copolymer containing 99.9 mol percent dimethylsiloxane units and 0.1 mol percent of methylvinylsiloxane units, was compounded in a conventional manner with 24 parts by weight of fume silica. The polymer-silica mixture was milled and 0.7 parts by weight of dichlorobenzoyl peroxide in the form of a paste in an equal amount of dimethylpolysiloxane was added and thoroughly dispersed through the mixture. This mixture was gum compound A.

Cerium oxide was mixed with an equal weight of dimethylpolysiloxane having a viscosity of 50,000 cs. at 25°C. to form a paste and the cerium oxide-dimethylpolysiloxane paste was mixed with sufficient gum compound A to form gum compound B containing 1000 ppm of cerium.

Gum compound C was within the scope of this invention and was prepared on a roll-mixer employing gum compound A and a sufficient amount of reaction product R_4 prepared as below to obtain 100 ppm of cerium in the gum compound.

Reaction product R_4 was prepared by admixing 40 g. of a mixture of hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane, 2.7 g. dimethylformamide and 2.8 g. sodium trimethylsilanolate, prepared by the method described by L. H. Sommer et al., Journal of the American Chemical Society, Vol. 68, page 2282, (1946), in solution in 10 g. of toluene. The mixture was heated at 105° to 110°C. for three hours. A mixture of 65 g. of xylene and 11.5 g. of cerous 2-ethylhexoate was added to the reaction mixture which was then heated at reflux temperature for three hours. The reaction mixture was cooled to room temperature and trimethyl-chlorosilane was added to neutralize any remaining sodium siloxanolate. Xylene, toluene and dimethylformamide were distilled off under reduced pressure. The generated precipitates were filtered off and the liquid reaction product R_4 was obtained. The reaction product R_4 contained 1.3% by weight of cerium.

The gum compounds A, B and C, were press-moulded at 120°C. for 10 minutes followed by a further cure in an air circulating oven at 250°C. for 1 hour. The silicone rubber samples so prepared were subjected to heat aging for 3 days in an air circulating oven heated at 250°C. to test the heat stability of the rubber. The tests were carried out under Japanese Industrial Standard C-2123. The results are tabulated below:

	Gum Compound	Durometer	Tensile Strength kg/cm²	Elongation %
A	Before heat aging	32	61	610
	After heat aging	73	41	43
B	Before heat aging	33	56	570
	After heat aging	34	54	430
C	Before heat aging	35	56	580
	After heat aging	37	54	440

As shown in the above table, the reaction product R_4 prepared in accordance with this disclosure containing 100 ppm of cerium gives an equivalent heat stabilizing effect to silicone rubber as cerium oxide containing 1000 ppm of cerium and reaction product R_4 is more easily dispersed uniformly throughout the rubber than is the cerium oxide.

WHAT WE CLAIM IS:—

1. A method for improving the heat stability of organopolysiloxanes which comprises adding thereto the reaction product of a cerium salt of an organic carboxylic acid which is soluble in an aromatic hydrocarbon solvent or a chlorinated hydrocarbon solvent with an alkali metal siloxanolate having an average of at least three organosiloxane units per molecule.

2. A method as claimed in claim 1 wherein the organopolysiloxane is an organosiloxane fluid or an organosiloxane elastomer.

3. A method as claimed in claim 1 or

2 wherein the cerium salt is cerium 2-ethylhexoate or cerium naphthoate.

4. A method as claimed in any of claims 1 to 3 wherein the alkali metal siloxanolate is potassium dimethylsiloxanolate, sodium dimethylsiloxanolate, potassium methylphenylsiloxanolate or sodium methylphenylsiloxanolate.

5. A method as claimed in any of claims 1 to 3 wherein the alkali metal siloxanolate is an essentially linear diorganosiloxane wherein the organic radicals bonded to silicon are methyl, ethyl, phenyl, vinyl or 3,3,3 - trifluoropropyl groups, one of the terminating units being an alkali metal siloxanolate unit and the other terminating unit being a triorganosiloxy unit wherein the organic substituents are as defined above.

6. A method as claimed in any of claims 1 to 5 wherein the reaction of the said cerium salt and the said siloxanote has been carried out in the presence of an aromatic hydrocarbon solvent or a chlorinated hydrocarbon solvent.

7. A method as claimed in any of claims 1 to 6 wherein the reaction of the said serium salt and the said siloxanolate has been carried out at the reflux temperature of the mixture.

8. A method as claimed in any of claims 1 to 7 wherein the ratio of the alkali metal siloxanolate to the cerium salt used is such that there are from 1 to 5 alkali metal siloxanolate units per cerium atom present.

9. A method as claimed in claim 1 substantially as described with reference to any of the Examples.

10. The reaction product of a serium salt of an organic carboxylic acid and an alkali metal siloxanolate having an average of at least three organosiloxane units per molecule.

11. A heat stabilized organopolysiloxane composition comprising an organosiloxane fluid or an organosiloxane elastomer containing as an additive, the reaction product of a cerium salt of an organic carboxylic acid and an alkali metal siloxanolate having an average of at least three organosiloxane units per molecule, wherein the additive is present in an amount to give from 0.01 to 1.0% by weight of cerium based on the weight of the total composition.

12. A heat stabilized organopolysiloxane composition as claimed in claim 11 wherein the additive is prepared by reacting a cerium salt of an organic carboxylic acid which is soluble in aromatic hydrocarbon solvents or chlorinated hydrocarbon solvents with a potassium or sodium siloxanolate.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1975
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.